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Novel Aluminum-Based, Transition Metal-Free, Catalytic Systems for Homo- and Copolymerization of Alkenes

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Since the initial reports by Ziegler[1] on the “aufbau” reaction, or stepwise insertion of ethene into the aluminum−carbon bond of alkylaluminum compounds, it has been widely believed that because of the accompanying displacement reaction the products of this reaction were limited to oligoethenes, with few reports of the preparation of high molecular weight polyethene at an aluminum center. Martin has described the preparation of polyethene by exposing ethene to a heptane solution of either bis(dichloroaluminum)ethane or trialkylaluminum over several days.[2] Recently, Jordan and Gibson have reported the polymerization of ethene using chelated alkylaluminum complexes activated by a Lewis acid.[3] On the other hand, the polymerization of higher alkenes, such as propene, by an aluminum-based system has ***never*** been reported. Herein, we report that high molecular weight, linear homo- and copolymers of ethene and propene can be prepared, in the absence of any transition metal species, via a catalyst system consisting of simple alkylaluminum compounds activated by Lewis acids.

The homo- and copolymerization of ethene and propene were carried out in 125 mL glass-lined reactors and our results are summarized in Tables 1−3. As can be seen, several systems based on the combination of an alkylaluminum compound and a Lewis acid are effective. Of note is the observation that methylaluminoxane (MAO) can act as either one of the two components (presumably because of the presence of small amounts of trimethylaluminum in the commercial sample). Several features of these systems are of interest. First, the molecular weights are high and ^{1}H and ^{13}C NMR spectroscopy indicates that the polymers are highly linear. The linearity of the polyethene formed was further supported by its high melting point ($T_m > 135$ °C). The polypropene is atactic. For the ethene−propene copolymer, the melting point was found to decrease with increasing propene content in the copolymer.

Narrow polydispersities (approximately 2) were observed for the polyethene and polypropene formed, suggesting a single-site catalyst. Finally, in the polymerization of ethene, the polymer molecular weight was found to increase with increasing reaction time (first entry in Table 1), indicating some degree of “livingness” to the system. This ***may*** be due to the lack of d-orbitals on aluminum that are necessary for chain transfer through facile β-hydrogen abstraction (β-hydrogen abstraction from neutral aluminum alkyls occurs only at elevated temperatures). The transfer of a growing polymer chain from a transition metal center to aluminum to form a stable aluminum-terminated polymer has been reported.[4]

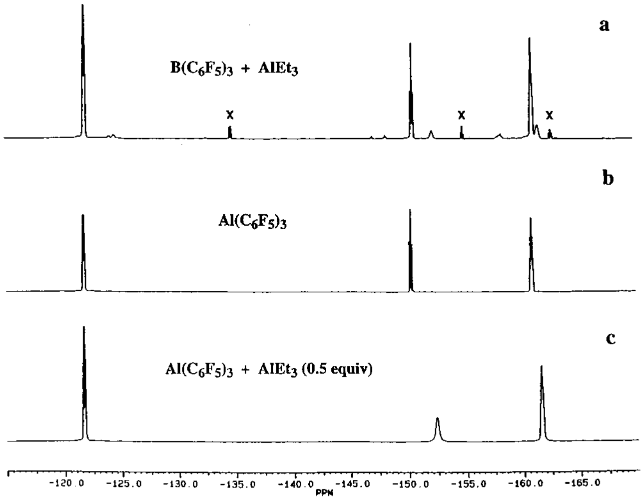

Figure 1. ^{19}F NMR spectra (C_6D_5Cl) of (a) $AlEt_3 + B(C_6F_5)_3$, (b) $Al(C_6F_5)_3$, and (c) $Al(C_6F_5)_3 + 0.5AlEt_3$. The resonances marked with X correspond to $C_6F_5{-}Et$. The resonances are referenced against CF_3COOH at −78.5 ppm.

A critically important issue that must be addressed for all transition metal-free polymerization systems is whether trace amounts of transition metal impurities are actually responsible for the polymerization. For reasons given below, this appears to be unlikely for the present systems. First, the two components used in our systems were analyzed for Ti, Zr, and V by AA spectroscopy and were found at levels less than the detection limit (<20 ppm). Second, any one of the components, when used alone, showed no polymerization activity (as anticipated slight polymerization activity was exhibited by MAO). Third, haloaluminum alkyl compounds, such as $AlEt_2Cl$ and $AlEtCl_2$, showed no activity when used either alone or with an activator such as MAO or $B(C_6F_5)_3$. Were the alkylaluminum compound simply activating a trace metal impurity, it seems likely that these compounds would show some activity. Fourth, single-site catalysts do not result from the combination of most transition metal salts and alkylaluminum compounds.

To probe the nature of the active species, the reactions of several trialkylaluminum compounds with $B(C_6F_5)_3$ were monitored by NMR spectroscopy (C_6D_5Cl).[5] In the ^{1}H NMR spectrum of tri-*n*-octylaluminum, the α-CH_2 attached to the aluminum appeared as a triplet at 0.7 ppm, the β-CH_2 appeared as a broad multiplet at 1.7 ppm, the terminal CH_3 appeared as a triplet at 1.1 ppm, and the remainder of the CH_2 units appeared as a broad resonance at 1.5 ppm. Following the addition of 1 equiv of $B(C_6F_5)_3$, the most significant change in the spectrum involved the shift of the α-CH_2 resonance from 0.7 to 1.8 ppm. The spectrum now corresponded to that of tri-*n*-octylboron as confirmed by its independent synthesis from $BH_3{\cdot}THF$ and 1-octene! Thus, as reported earlier,[5] a near-quantitative exchange of organic groups had occurred between aluminum and boron to form trialkylboron and $Al(C_6F_5)_3$. The same conclusion was also reached from an examination of the ^{13}C NMR spectrum of the reaction mixture. Very similar results were also obtained with triethylaluminum. Moreover, neither the combinations, triethylboron and $B(C_6F_5)_3$ (1:1) or triethylboron and triethylaluminum (1:1), nor $Al(C_6F_5)_3$[6] alone catalyzed the polymerization of ethene.

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Table 1. Polymerization of Ethene

catalyst components (mmol)		solvent	yield (g)	activity (kg/mol·h)[e]	M_n[f] ($\times 10^{-3}$)	M_w[f] ($\times 10^{-3}$)
$AlEt_3$ (0.3)	MAO (0.3)	C_6H_5Cl	3.9[a]	3.25	40 (111)[b]	98 (263)[b]
$AlEt_3$ (0.3)	MAO (0.3)	toluene	0.6[a]	0.50		
MAO (0.3)	$B(C_6F_5)_3$ (0.3)	C_6H_5Cl	0.4[a]	0.35	262	485
$AlEt_3$ (0.3)	$B(C_6F_5)_3$ (0.3)	C_6H_5Cl	1.0[a]	0.85		
$AlEt_3$ (0.3)	Trityl FAB (0.3)	C_6H_5Cl	2.8[a]	2.33		
$AlMe_3$ (0.3)	MAO (0.3)	C_6H_5Cl	1.5[a]	1.25		
$(i\text{-}Bu)_2AlH$ (0.3)	$B(C_6F_5)_3$ (0.3)	C_6H_5Cl	0.6[a]	0.50		
$(i\text{-}Bu)_2AlH$ (0.3)	An. FAB (0.3)	C_6H_5Cl	0.5[a]	0.41		
$AlEt_3$ (0.08)	An. FAB (0.08)	C_6H_5Cl	1.1[c]	13.75		
$Al(i\text{-}Bu)_3$ (0.12)	An. FAB (0.06)	C_6H_5Cl	0.4[d]	2.22		

[a] 20 mL of solvent, 800 psi of ethene, 50 °C, 4 h. [b] 20 h. [c] 10 mL of solvent, 800 psi of ethene, 50 °C, 1 h. [d] 10 mL of solvent, 800 psi of ethene, 50 °C, 1.5 h. [e] Relative to Al (first component). [f] Relative to polystyrene standards. MAO: methylaluminoxane. Trityl FAB: $[(C_6H_5)_3C][B(C_6F_5)_4]$. An. FAB: $[(C_6H_5)N(CH_3)_2H][B(C_6F_5)_4]$.

Table 2. Polymerization of Propene[a]

catalyst components		solvent	yield (g)	activity (kg/mol·h)[b]	M_n[c] ($\times 10^{-3}$)	M_w[c] ($\times 10^{-3}$)
$AlEt_3$	$B(C_6F_5)_3$	C_6H_5Cl	0.71	0.12	74	140
MAO	$B(C_6F_5)_3$	toluene	0.95	0.16	112	229
$AlMe_3$	$B(C_6F_5)_3$	C_6H_5Cl	0.20	0.03		

[a] Reaction Conditions: 0.3 mmol of each catalyst component, 10 mL of solvent, 5 g of propene, 50 °C, 20 h. [b] Relative to Al (first component). [c] Relative to polystyrene standards. MAO: methylaluminoxane.

Table 3. Copolymerization of Ethene and Propene[a]

ethene (psi)	propene (psi)	time (h)	yield (g)	propene incorporation (%)	T_m (°C)
700	0	1.5	1.84	0	135.9
400	100	5	4.39	4.67	121.6
300	100	5	2.50	5.40	115.5
150	100	5	0.70	5.88	108.5
50	100	5	0.05	16.9	53.4

[a] Reaction conditions for each run: 0.1 mmol each of $AlEt_3$ and $[(C_6H_5)N(CH_3)_2H][B(C_6F_5)_4]$, 10 mL of C_6H_5Cl, single charge of monomers, 60 °C.

Table 4. Polymerization of Ethene as a Function of $Al(C_6F_5)_3{\cdot}0.5$Toluene:$AlEt_3$ Ratio[a]

$Al(C_6F_5)_3{\cdot}0.5$ toluene (μmol)	$AlEt_3$ (equiv)	yield (g)	activity[b] (kg/mol·h)
80	0.3	0.27	3.4
80	0.5	0.87	10.9
80	0.9	0.08	1.0
80	1.2	0.20	2.5
80	2.0	0.14	1.8

[a] Reaction conditions: 15 mL of C_6H_5Cl, 700 psi of ethene, 60 °C, 1 h. [b] Based on $Al(C_6F_5)_3{\cdot}0.5$ toluene.

Clearly, the search for the active catalyst formed from triethylaluminum and $B(C_6F_5)_3$ must lie elsewhere.

The ^{19}F NMR spectrum of a 1:1 mixture of triethylaluminum and $B(C_6F_5)_3$ was dominated by resonances due to $Al(C_6F_5)_3$ (Figure 1a,b). However, there was a second (minor) set of C_6F_5 resonances (Figure 1a). The *p*- and *m*-fluorines resonated at −154.5 (br) and −163.0 ppm (br). The resonance due to *o*-fluorine atoms overlapped with the peak from the *o*-fluorine atoms of $Al(C_6F_5)_3$. ***Only the resonances corresponding to the second species was obtained when $Al(C_6F_5)_3{\cdot}0.5$ toluene was combined with 0.5 equiv of triethylaluminum in C_6D_5Cl (Figure 1c).*** While the exact nature of this species remains uncertain, it is clearly a mixed alkyl, perfluorophenyl complex of aluminum, $[(Et)(C_6F_5)_2Al]_x$.[6] Moreover, as shown in Table 4, when ethene was polymerized using varying ratios of $Al(C_6F_5)_3{\cdot}0.5$ toluene and $AlEt_3$, the highest activity was observed for a 1:0.5 ratio of the two components suggesting that $[(Et)(C_6F_5)_2Al]_x$ is the actual catalyst or its direct precursor.

In conclusion, we have demonstrated that simple alkylaluminum compounds, when activated by suitable Lewis acids, are capable of catalyzing the homo- and copolymerization of ethene and propene to high molecular weight polymers with narrow polydispersities.

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